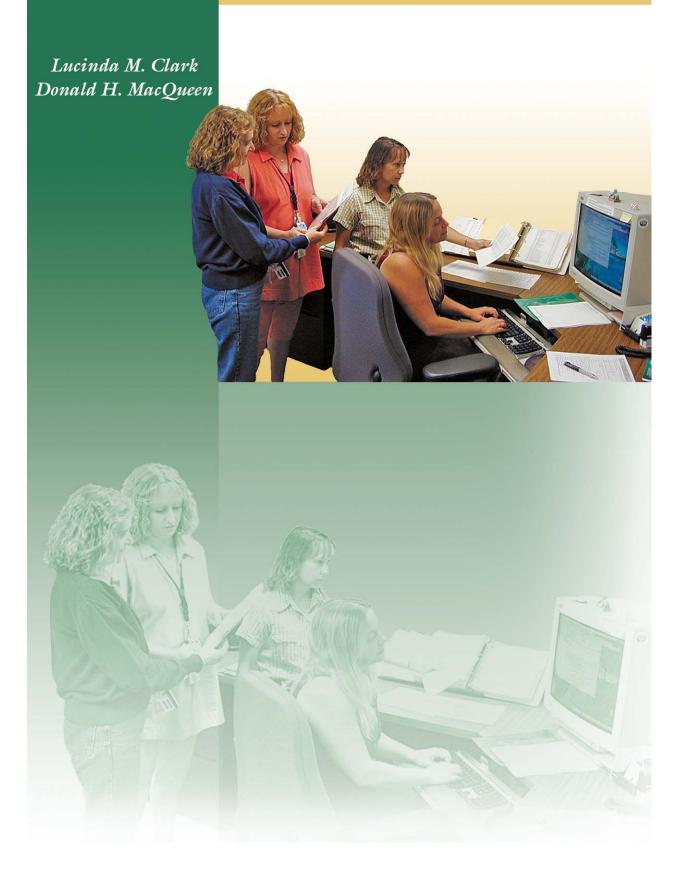


Quality Assurance



INTRODUCTION

Quality assurance (QA) is a system of activities and processes put in place to ensure that products or services meet or exceed customer specifications. Quality control (QC) consists of activities used to verify that deliverables are of acceptable quality and meet criteria established in the quality planning process. Lawrence Livermore National Laboratory conducted environmental monitoring activities during 2003 in accordance with the Environmental Protection Department Quality Assurance Management Plan (Revision 4), which is based on DOE Order 414.1A. This order sets forth policy, requirements, and responsibilities for the establishment and maintenance of plans and actions that assure quality in DOE programs using a risk-based, graded approach to QA. This process promotes the selective application of QA and management controls based on the risk associated with each activity in order to maximize effectiveness and efficiency in resource use.

LLNL and commercial laboratories analyze environmental monitoring samples using U.S. Environmental Protection Agency (EPA) standard methods when available. When EPA standard methods are not available, custom analytical procedures, usually developed at LLNL, are used. LLNL uses only State of California-certified laboratories to analyze its environmental monitoring samples. In addition, LLNL requires all analytical laboratories to maintain adequate QA programs and documentation of methods. The radiochemical methods used by LLNL laboratories are described in procedures created and maintained by the laboratory performing the analyses.

QUALITY ASSURANCE ACTIVITIES

Nonconformance reporting and tracking is a process used for ensuring that problems are identified, resolved, and prevented from recurring. EPD reports and tracks problems using Nonconformance Reports (NCRs) and Analytical Lab Problem Reporting Forms.

The LLNL Environmental Protection Department (EPD) generated 31 NCRs and 3 Analytical Lab Problem Reporting Forms related to environmental monitoring in 2003. Ten of the 31 NCRs generated in 2003 documented routine equipment maintenance. Of the remaining 24 problems reported, 9 were due to documentation, procedural, or sampling errors; 7 were due to problems with analytical laboratories; 7 were related to equipment malfunction; and 1 was related to sediment sampling locations that had been chronically difficult to sample (these sampling locations were eliminated based on this NCR, but will be reevaluated in the future as conditions change or new sampling methodology becomes available).

LLNL addresses internal documentation, training, and procedural errors by conducting formal and informal training. These errors generally do not result in lost samples, but may require extra work on the part of sampling and data management personnel to resolve or compensate for the errors.

LLNL addresses analytical laboratory problems with the appropriate laboratory as they arise. Many of the documented problems related to analytical laboratories concerned minor documentation or paperwork errors, which were corrected soon after they were identified. Other problems—such as missed holding times, late analytical results, and typographical errors on data reports—accounted for the remaining analytical laboratory issues. These problems were corrected by reanalysis, resampling, reissued reports, or corrected paperwork, and associated sample results were not affected.

QA staff also track and report planned environmental monitoring samples that are not collected. A summary of these lost samples appears in **Table 8-1**.

Table 8-1. Sampling completeness in 2003 for the Livermore site and Site 300

Environmental medium	Number of analyses planned	Number of analyses completed	Completeness (%)	Reason(s) for lost samples
Air particulate				
Radiological parameters (Livermore site)	1188	1161	98	No power at location (21), sampler malfunction (6)
Beryllium (Livermore site)	96	96	100	
Radiological parameters (Site 300)	728	722	99	No power at location (4), access to location denied (1), cable cut (1)
Beryllium (Site 300)	48	48	100	
Air tritium				
Livermore site	536	525	98	Total flow too low (9), flow meter malfunction (2)
Site 300	29	28	97	Flow meter malfunction (1)
Soil and Sediment				
Livermore site	42	42	100	
Site 300	30	30	100	
Arroyo sediment (Livermore site only)	43	43	100	
Vegetation and Foodstuffs				
Livermore site and vicinity	64	64	100	
Site 300	20	20	100	
Wine	25	25	100	

Table 8-1. Sampling completeness in 2003 for the Livermore site and Site 300 (continued)

Environmental medium	Number of analyses planned	Number of analyses completed	Completeness (%)	Reason(s) for lost samples
Thermoluminescent dosimeters (TLDs)				
Livermore site perimeter	76	72	95	TLD missing at pickup time (4)
Livermore Valley	100	94	94	TLD missing at pickup time (6)
Site 300	64	61	95	TLD missing at pickup time (3)
Rain ^(a)				
Livermore site	53	53	100	
Site 300	9	4	44	Insufficient rainfall to collect sample (5)
Storm water runoff ^(a)				
Livermore site	390	379	97	Location inaccessible due to construction (9), sample cancelled (2)
Site 300	226	0	0	Insufficient runoff
Drainage Retention Basin				
Field measurements	229	226	99	Measurements overlooked (3)
Samples	72	72	100	
Releases	72	72	100	
Groundwater				
Livermore site	298	296	99	Samples not scheduled (2)
Livermore Valley	25	23	92	Vendor did not provide requested samples (2)
Site 300				
Building 829 network	202	188	93	Well dry (14)
Elk Ravine	169	153	91	Well dry (15), sampling error (1)
Pit 1	432	432	100	
Pit 6	289	268	93	Well dry (20), sampling error (1)
Pit 7	429	429	100	
Off-site surveillance (annual)	70	70	100	
Off-site surveillance (quarterly)	136	129	95	Sampling error (7)
Well 20	38	37	97	Sampling error (1)

Table 8-1. Sampling completeness in 2003 for the Livermore site and Site 300 (continued)

Environmental medium	Number of analyses planned	Number of analyses completed	Completeness (%)	Reason(s) for lost samples
Livermore site wastewater				
B196	925	921	99	Power cut to sampler (2), sample not collected (2)
C196	326	324	99	Automatic sampler malfunction (2)
LWRP ^(b) effluent	48	48	100	
Digester sludge	80	80	100	
WDR 96-248				
Surface impoundment wastewater	56	54	96	pH values not reported (2)
Surface impoundment groundwater	160	160	100	
Sewage ponds wastewater	35	34	97	Analytical laboratory error (1)
Sewage ponds groundwater	80	80	100	
Miscellaneous aqueous samples				
Other surface water (Livermore Valley only)	58	58	100	
Cooling towers (Site 300 only)	24	24	100	

a Numbers for Livermore site runoff and Site 300 rain are for the three storms that were sampled. The goal is to sample four storms per year; however, there was insufficient rainfall during routine work hours to sample four storms during 2003.

ANALYTICAL LABORATORIES

LLNL continued to operate under the Blanket Service Agreements (BSAs) put into place with seven analytical laboratories in March 1999. LLNL continues to work closely with these analytical laboratories to minimize the occurrence of problems.

b LWRP = Livermore Water Reclamation Plant

Analytical Laboratory Intercomparison Studies

LLNL uses the results of intercomparison program data to identify and monitor trends in performance and to solicit corrective action responses for unacceptable results. If a laboratory performs unacceptably for a particular test in two consecutive performance evaluation studies, LLNL may choose to select another laboratory to perform the affected analyses until the original laboratory can demonstrate that the problem has been corrected. If an off-site laboratory continues to perform unacceptably or fails to prepare and implement acceptable corrective action responses, the LLNL Procurement Department will formally notify the laboratory of its unsatisfactory performance. If the problem persists, the off-site laboratory's BSA could be terminated. If an on-site laboratory continues to perform unacceptably, use of that laboratory could be suspended until the problem is corrected.

Two laboratories at Lawrence Livermore National Laboratory participated in the annual Environmental Monitoring Laboratory (EML) intercomparison studies program sponsored by the U.S. Department of Energy (DOE). The two LLNL laboratories are the Environmental Radiochemistry Environmental Monitoring Radiological Laboratory (EMRL) and the Hazards Control Department's Analytical Laboratory (HCAL).

The results of EMRL's participation in the 2003 EML studies are presented in Table 8-2. According to the results, 26 of 41 reported results were determined to be acceptable, 8 results were acceptable with warning, and 7 results were unacceptable, based on established control limits. Five of the unacceptable results were due to data entry errors and results were acceptable once the errors were corrected. The remaining two unacceptable results were due to differences between calibration samples and actual test samples. The root cause for the results acceptable with warning and unacceptable results were examined and procedures were put in place to prevent them from re-occurring.

The results of HCAL's participation in the 2003 EML studies (see **Table 8-3**) indicate that 6 of 10 sample results fell within the 3σ acceptance control limits, three results fell in the acceptable with warning range, and one result was unacceptable (high). The Gross Alpha as performed at the HCAL has a known positive bias because of differences between the calibration nuclide and the test nuclide.

EMRL participated in two DOE Mixed Analyte Performance Evaluation Program (MAPEP) studies in 2002. The results of these studies are presented in **Tables 8-4** and **8-5**. Nineteen of 20 analytes reported by EMRL in these studies fell within acceptable limits; the remaining value was acceptable with warning.

Although contract laboratories are also required to participate in laboratory intercomparison programs, permission to publish their results for comparison purposes was not granted for 2003. See the following website for contract laboratory results: $\frac{1}{\text{www.eml.doe.gov}} = \frac{1}{\text{QAP}}.$

Table 8-2. EMRL results from the DOE EML Quality Assurance Program, 2003

Analyte	EML study	EMRL value	EML value	EMRL/ EML	Control limits ^(a,b)	Warning limits ^(a,b)	Performance ^(a,b)			
Air filter (Bq/filter)										
Co-60	QAP 58	44.1	33.5	1.32	0.80 – 1.26	0.90 – 1.11	Not Acceptable			
	QAP 59	60.0	55.1	1.09	0.80 – 1.26	0.90 – 1.11	Acceptable			
Cs-137	QAP 58	136	99.7	1.36	0.80 – 1.32	0.90 – 1.17	Not Acceptable			
	QAP 59	101	54.8	1.84	0.80 – 1.32	0.90 – 1.17	Not Acceptable			
Gross alpha	QAP 58	1.15	1.17	0.983	0.73 – 1.43	0.84 – 1.21	Acceptable			
	QAP 59	3.5	3.11	1.12	0.73 – 1.43	0.84 – 1.21	Acceptable			
Gross beta	QAP 58	1.64	1.50	1.09	0.76 – 1.36	0.85 – 1.21	Acceptable			
	QAP 59	4.04	3.89	1.04	0.76 – 1.36	0.85 – 1.21	Acceptable			
Mn-54	QAP 58	61.1	43.8	1.40	0.80 – 1.35	0.90 – 1.19	Not Acceptable			
	QAP 59	76.4	58.0	1.32	0.80 – 1.35	0.90 – 1.19	Warning			
Pu-238	QAP 58	0.507	0.520	0.975	0.67 – 1.33	0.88 – 1.12	Acceptable			
	QAP 59	0.249	0.229	1.09	0.67 – 1.33	0.88 – 1.12	Acceptable			
Ρυ-239	QAP 58	0.319	0.330	0.967	0.73 – 1.26	0.88 – 1.12	Acceptable			
	QAP 59	0.427	0.401	1.06	0.73 – 1.26	0.88 – 1.12	Acceptable			
				Soil (Bq	/kg)					
Cs-137	QAP 58	1290	1450	0.89	0.80 – 1.25	0.90 – 1.16	Warning			
	QAP 59	1520	1973	0.770	0.80 – 1.25	0.90 – 1.16	Not Acceptable			
K-40	QAP 58	594	636	0.934	0.80 – 1.32	0.90 – 1.19	Acceptable			
	QAP 59	409	488	0.838	0.80 – 1.32	0.90 – 1.19	Warning			
Pu-238	QAP 58	0.891	21.9	0.041	0.59 - 2.88	0.87 – 1.49	Not Acceptable			
	QAP 59	15.9	14.6	1.09	0.59 – 2.88	0.87 – 1.49	Acceptable			
Pu-239	QAP 58	0.947	23.4	0.040	0.71 – 1.30	0.87 – 1.13	Not Acceptable			
	QAP 59	36.1	30.4	1.19	0.71 – 1.30	0.87 – 1.13	Warning			
				Water (E	Sq/L)					
Am-241	QAP 58	2.26	2.13	1.06	0.79 – 1.41	0.90 – 1.19	Acceptable			
Co-60	QAP 58	246	234	1.05	0.80 – 1.20	0.90 – 1.10	Acceptable			
	QAP 59	508	513	0.990	0.80 – 1.20	0.90 – 1.10	Acceptable			
Cs-134	QAP 58	24.6	30.5	0.807	0.80 – 1.30	0.90 – 1.14	Warning			
	QAP 59	53.4	63.0	0.848	0.80 – 1.30	0.90 – 1.14	Warning			
Cs-137	QAP 58	65.4	63.8	1.03	0.80 – 1.22	0.90 – 1.12	Acceptable			
	QAP 59	84.5	50.3	1.05	0.80 – 1.22	0.90 – 1.12	Acceptable			
Gross alpha	QAP 58	222	378	0.588	0.58 – 1.29	0.79 – 1.13	Warning			
	QAP 59	610	622	0.981	0.58 – 1.29	0.79 – 1.13	Acceptable			

Table 8-2. EMRL results from the DOE EML Quality Assurance Program, 2003(continued)

Analyte	EML study	EMRL value	EML value	EMRL/ EML	Control limits ^(a,b)	Warning Iimits ^(a,b)	Performance ^(a,b)
Gross beta	QAP 58	618	626	0.985	0.61 – 1.43	0.81 – 1.29	Acceptable
	QAP 59	1880	1948	0.965	0.61 – 1.43	0.81 – 1.29	Acceptable
H-3	QAP 58	395	390	1.01	0.78 - 2.45	0.90 – 1.32	Acceptable
	QAP 59	537	446	1.20	0.78 - 2.45	0.90 – 1.32	Acceptable
Pu-238	QAP 58	3.68	3.33	1.10	0.74 – 1.20	0.90 – 1.10	Warning
	QAP 59	2.25	2.07	1.09	0.74 – 1.20	0.90 – 1.10	Acceptable
Pu-239	QAP 58	4.26	3.92	1.09	0.79 – 1.20	0.90 – 1.10	Acceptable
	QAP 59	5.49	4.99	1.10	0.79 – 1.20	0.90 – 1.10	Acceptable
U-234	QAP 58	1.96	2.05	0.956	0.80 – 1.34	0.90 – 1.16	Acceptable
U-238	QAP 58	1.96	2.16	0.907	0.80 – 1.28	0.90 – 1.16	Acceptable

a Control and warning limits are established from historical QAP data and reported as the ratio of reported value to EML value. The criteria for acceptable performance is between the 15th and the 85th percentiles of the cumulative normalized distribution. The acceptable with warning criteria is between the 5th and the 15th percentiles and between the 85th and 95th percentiles. Values less than the 5th and greater than the 95th percentiles are not acceptable.

Table 8-3. HCAL results from the DOE EML Quality Assurance Program, 2003

Analyte	EML study	HCAL value	EML value	HCAL/ EML	Control limits ^(a,b)	Warning limits ^(a,b)	Performance ^(a,b)
			A	Air filter (Bq/	/filter)		
Gross alpha	QAP 58	1.62	1.17	1.38	0.73 – 1.43	0.84 – 1.21	Warning
	QAP 59	4.24	3.11	1.36	0.73 – 1.43	0.84 – 1.21	Warning
Gross beta	QAP 58	1.70	1.5	1.13	0.76 – 1.36	0.85 – 1.21	Acceptable
	QAP 59	4.23	3.89	1.09	N/A yet	N/A yet	Acceptable
				Water (Bq	/L)		
Gross Alpha	QAP 58	455	378	1.20	0.58 – 1.29	0.79 – 1.13	Warning
	QAP 59	469	446	1.05	0.58 – 1.29	0.79 – 1.13	Acceptable
Gross Beta	QAP 58	705	628	1.12	0.61 – 1.43	0.81 – 1.29	Acceptable
	QAP 59	857	622	1.38	0.61 – 1.43	0.81 – 1.29	Not Acceptable
Tritium	QAP 58	407	390	1.04	0.78 - 2.45	0.90 – 1.32	Acceptable
	QAP 59	2039	1948	1.05	N/A yet	N/A yet	Acceptable

a Control and warning limits are established from historical QAP data and reported as the ratio of reported value to EML value. The criteria for acceptable performance is between the 15th and the 85th percentiles of the cumulative normalized distribution. The acceptable with warning criteria is between the 5th and the 15th percentiles and between the 85th and 95th percentiles. Values less than the 5th and greater than the 95th percentiles are not acceptable.

b The EML program was cancelled after study QAP 60 and control limits were not recalculated for QAP 59 or QAP 60. Control limits from the QAP 58 study were used to evaluate QAP 59 results.

b The EML program was cancelled after study QAP 60 and control limits were not recalculated for QAP 59 or AQP 60. Control limits from the QAP 58 study were used to evaluate QAP 59 results.

Table 8-4. EMRL performance in the MAPEP-02-W10 Intercomparison Program for Water

Analyte	EMRL value	Units	Reference value	Bias (%)	Acceptance range	Performance ^(a)
Americium-241	0.543	Bq/L	0.578	-6.1	0.40 –.075	Acceptable
Cesium-134	355	Bq/L	421	-15.7	295 – 547	Acceptable
Cesium-137	317	Bq/L	329	-3.6	230 – 428	Acceptable
Cobalt-57	57.1	Bq/L	57	0.2	39.9 – 74.1	Acceptable
Cobalt-60	39.1	Bq/L	38.2	2.4	26.7 – 49.7	Acceptable
Manganese-54	35.3	Bq/L	32.9	7.3	23.0 – 42.8	Acceptable
Plutonium-238	0.791	Bq/L	0.828	-4.5	0.58 – 1.08	Acceptable
Plutonium-239/240	0.0105	Bq/L	_	_	_	Acceptable
Uranium-234/233	1.36	Bq/L	1.54	-11.7	1.08 – 2.00	Acceptable
Uranium-238	1.38	Bq/L	1.6	-13.8	1.12 – 2.08	Acceptable
Zinc-65	555	Bq/L	516	7.6	361 – 671	Acceptable

a Acceptable results have bias ≤20%. Results acceptable with warning have basis >20% and bias ≤30%. Results with basis >30% are not acceptable..

Table 8-5. EMRL performance in the MAPEP-03-S10 Intercomparison Program for Soil

Analyte	EMRL value	Units	Reference value	Bias (%)	Acceptance range	Performance ^(a)
Cesium-134	188	Bq/kg	238	-21.0	167 – 309	Warning
Cesium-137	812	Bq/kg	832	-2.4	582 – 1080	Acceptable
Cobalt-57	541	Bq/kg	530	2.1	391 – 689	Acceptable
Cobalt-60	424	Bq/kg	420	1.0	294 – 546	Acceptable
Manganese-54	145	Bq/kg	137	5.8	95.9 – 178	Acceptable
Plutonium-238	65.2	Bq/kg	66.9	-2.5	46.8 – 87.0	Acceptable
Plutonium-239/240	50.4	Bq/kg	52.7	-4.4	36.9 – 68.5	Acceptable
Potassium-40	725	Bq/kg	652	11.2	456 – 848	Acceptable
Zinc-65	562	Bq/kg	490	14.7	343 – 637	Acceptable

a Acceptable results have bias ≤20%. Results acceptable with warning have basis >20% and bias ≤30%. Results with basis >30% are not acceptable.

DUPLICATE ANALYSES

Duplicate or collocated samples are distinct samples of the same matrix collected as closely to the same point in space and time as possible. Collocated samples processed and analyzed by the same laboratory provide intralaboratory information about the precision of the entire measurement system, including sample acquisition, homogeneity, handling, shipping, storage, preparation, and analysis. Collocated samples processed and analyzed by different laboratories provide interlaboratory information about the precision of the entire measurement system (U.S. EPA 1987). Collocated samples may also be used to identify errors such as mislabeled samples or data entry errors.

Tables 8-6, **8-7**, and **8-8** present statistical data for collocated sample pairs, grouped by sample matrix and analyte. Samples from both the Livermore site and Site 300 are included. **Tables 8-6** and **8-7** are based on data pairs in which both values are detections (see "Data Presentation"). **Table 8-8** is based on data pairs in which either or both values are nondetections.

Precision is measured by the percent relative standard deviation (%RSD); see the EPA's Data Quality Objectives for Remedial Response Activities: Development Process, Section 4.6 (U.S. EPA 1987). Acceptable values for %RSD vary greatly with matrix, analyte, and analytical method; however, lower values represent better precision. The results for %RSD given in **Table 8-6** are the 75th percentile of the individual precision values.

Regression analysis consists of fitting a straight line to the collocated sample pairs. Good agreement is indicated when the data lie close to a line with a slope equal to 1 and an intercept equal to 0, as illustrated in **Figure 8-1**. Allowing for normal analytical variation, the slope of the fitted line should be between 0.7 and 1.3, and the absolute value of the intercept should be less than the detection limit. The coefficient of determination (r^2) should be greater than 0.8. These criteria apply to pairs in which both results are above the detection limit.

When there were more than eight data pairs with both results in each pair considered detections, precision and regression analyses were performed; those results are presented in **Table 8-6**. When there were eight or fewer data pairs with both results above the detection limit, the ratios of the individual duplicate sample pairs were averaged; the mean, minimum, and maximum ratios for selected analytes are given in **Table 8-7**. The mean ratio should be between 0.7 and 1.3. When either of the results in a pair is a nondetection, then the other result should be a nondetection or less than two times the detection limit. **Table 8-8** identifies the sample media and analytes for which at least one pair failed this criterion. Media and analytes with fewer than four pairs are omitted from the table.

Collocated sample comparisons are more variable when the members of the pair are analyzed by different methods or with different criteria for analytical precision. For example, radiological analyses using different counting times or different laboratory

aliquot sizes will have different amounts of variability. Different criteria are rarely, if ever, used with collocated sample pairs in LLNL environmental monitoring sampling. Different criteria are sometimes used in special studies when more than one regulatory agency is involved.

Table 8-6. Quality assurance collocated sampling: Summary statistics for analytes with more than eight pairs in which both results were above the detection limit

Media	Analyte	N ^(a)	%RSD ^(b)	Slope	r ^{2(c)}	Intercept
Air	Gross alpha (variability) ^(d)	84	57.8	0.42	0.28	$2.33 \times 10^{-5} \text{ (Bq/m}^3\text{)}$
	Gross beta (variability) ^(d)	95	20	0.767	0.58	$5.37 \times 10^{-5} \text{ (Bq/m}^3\text{)}$
	Beryllium	12	11.8	1.03	0.97	-0.252 (pg/m ³)
	Uranium-235 (outliers) ^(e)	12	5.56	0.409	0.52	$7.92 \times 10^{-8} (\mu \text{g/m}^3)$
	Uranium-238 (outliers) ^(e)	12	5.39	0.413	0.53	$1.08 \times 10^{-5} (\mu \text{g/m}^3)$
	Tritium	28	18.8	1.05	1	0.0344 (Bq/m ³)
Dose (TLD)	90-day radiological dose	30	2.89	0.949	0.91	0.72 (mrem)
Groundwater	Gross beta	21	14.1	0.953	0.97	0.00155 (Bq/L)
	Arsenic	17	4.29	1.02	1	-0.000278 (mg/L)
	Barium	12	3.73	1.06	1	-0.00203 (mg/L)
	Bromide	9	15.7	1.02	0.84	-0.0206 (mg/L)
	Chloride	9	0.344	1	1	0.386 (mg/L)
	Nitrate (as NO3)	18	3.2	0.972	0.98	1.72 (mg/L)
	Ortho-Phosphate	10	5.18	0.895	0.94	0.0132 (mg/L)
	Potassium	24	2.26	0.99	0.98	0.361 (mg/L)
	Sulfate	9	0.369	1	1	-0.0905 (mg/L)
	Tritium	13	5.83	0.99	1	-2.47 (Bq/L)
	Uranium-234+233	13	8.81	0.835	0.99	0.0092 (Bq/L)
	Uranium-235+236	10	23.3	0.907	0.95	0.000109 (Bq/L)
	Uranium-238	13	9.03	0.903	0.99	0.00532 (Bq/L)
Sewer	Gross alpha (variability) ^(d)	20	39.1	0.526	0.46	8.04 × 10 ⁻⁵ (Bq/mL)
	Gross beta	53	8.81	0.948	0.88	$6.06 \times 10^{-5} \text{ (Bq/mL)}$

a Number of collocated pairs included in regression analysis

b 75th percentile of percent relative standard deviations (%RSD) where %RSD = $\left(\frac{200}{\sqrt{2}}\right)\frac{|x_1-x_2|}{x_1+x_2}$ and x_1 and x_2 are the reported concentrations of each routine-duplicate pair

c Coefficient of determination

d Outside acceptable range of slope or r² because of variability

e Outside acceptable range of slope or r² because of outliers

Table 8-7. Quality assurance collocated sampling: Summary statistics for selected analytes with eight or fewer pairs in which both results were above the detection limit

Media	Analyte	N ^(a)	Mean ratio	Minimum ratio	Maximum ratio
Aqueous	Gross beta	1	0.97	0.97	0.97
Drinking water	Gross beta	1	2	2	2
Groundwater	Gross alpha	7	0.95	0.56	1.8
	Radium-226	6	1.3	0.78	2
	Thorium-228	1	0.45	0.45	0.45
Runoff	Gross alpha	2	1.1	0.92	1.2
(from rain)	Gross beta	3	0.89	0.81	0.94
	Tritium	1	1.1	1.1	1.1
Soil	Cesium-137	3	0.89	0.69	1.1
	Tritium	1	2	2	2
	Tritium	1	1.9	1.9	1.9
	Potassium-40	4	1	0.97	1.1
	Plutonium-238	2	1.4	1.3	1.6
	Plutonium-239+240	3	1	0.51	1.4
	Radium-226	4	1	0.98	1
	Radium-228	4	1	0.97	1
	Thorium-228	4	0.99	0.87	1
	Uranium-235	4	1.1	0.79	1.4
	Uranium-238	4	0.91	0.75	1.1
Vegetation	Tritium	4	1.3	0.94	2

a Number of collated pairs used in ratio calculations

Table 8-8. Quality assurance collocated sampling: Summary statistics for analytes with at least four pairs in which one or both results were below the detection limit.

Media	Analyte	Number of inconsistent pairs	Number of pairs	Percent of inconsistent pairs
Air	Gross beta	6	7	86
	Plutonium-238	1	12	8.3
	Plutonium-239+240	2	24	8.3
	Tritium	2	22	9.1
Groundwater	Total organic halides	1	4	25
Sewer	Gross alpha	5	33	15
	Benzene	1	6	17

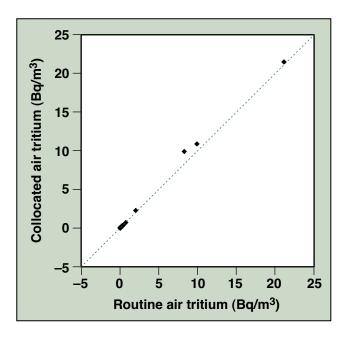


Figure 8-1. Example of data points that lie close to a line with slope equal to 1 and intercept equal to 0 using air tritium concentrations from collocated samples

Routine and collocated sample results show fairly good agreement: 90% of the pairs have a precision of 43% or better. Data sets not meeting our precision criteria fall into one of two categories. The first category, outliers, can occur because of data transcription errors, measurement errors, or real but anomalous results. Of the 22 data sets reported in Table 8-6, two did not meet the criterion for acceptability because of outliers. Figure 8-2 illustrates a set of collocated pairs with one outlier.

The second category is data sets that do not meet the criterion for acceptability because results are highly variable. This tends to be typical of nondetections and measurements at extremely low concentrations, as illustrated in **Figure 8-3**. Low concentrations of radio-nuclides on particulates in air highlight this effect, because a small number or radio-nuclide-containing particles on an air filter can significantly affect results. Other causes of high variability are sampling and analytical methodology. Analyses of total organic carbon and total organic halides in water are particularly difficult to control. Of the 22 data sets in **Table 8-7**, three show sufficient variability in results to make them fall outside the acceptable range.

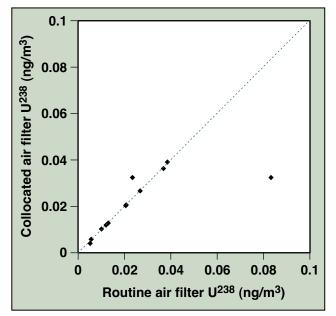


Figure 8-2. Example of data with an outlier using air filter uranium-238 concentrations from collocated samples

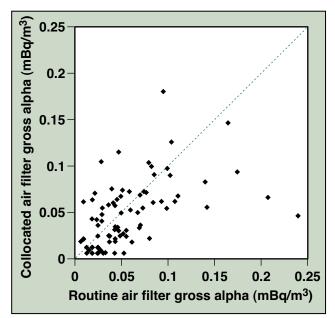


Figure 8-3. Example of variability using air filter gross alpha concentrations from collocated samples

DATA PRESENTATION

Most data tables provided in the report CD were created using computer scripts that retrieve data from the database, convert to SI units when necessary, calculate summary statistics for tables that include summary statistics, format data as appropriate, lay out the table into the desired rows and columns, and present a draft table. Final tables are included after review by the responsible analyst. Analytical laboratory data, and values calculated from analytical laboratory data, are normally displayed with two or at most three significant digits. Significant trailing zeros may be omitted.

Radiological Data

Most of the data tables display radiological data as a result plus-or-minus an associated 2σ uncertainty. The uncertainties are not used in summary statistic calculations. Any radiological result exhibiting a 2σ uncertainty greater than or equal to 100% of the result is considered to be a nondetection.

Some radiological results are derived from the number of sample counts minus the number of background counts inside the measurement apparatus. Therefore, a sample with a low concentration may have a negative value; such results are reported in the tables and used in the calculation of summary statistics and statistical comparisons.

Some data tables provide a limit-of-sensitivity value instead of an uncertainty when the radiological result is below the detection criterion. Such results are displayed with the limit-of-sensitivity value in parentheses.

Nonradiological Data

Nonradiological data reported by the analytical laboratory as being below the reporting limit are displayed in tables with a less-than symbol. The reporting limit values are used in the calculation of summary statistics, as explained below.

STATISTICAL COMPARISONS AND SUMMARY STATISTICS

Standard comparison techniques (such as regression, t-tests, and analysis of variance) have been used where appropriate to determine the statistical significance of trends or differences between means. When such a comparison is made, it is explicitly stated in the text as being "statistically significant" or "not statistically significant." Other uses of the word "significant" in the text do not imply that statistical tests have been performed. Instead, these uses relate to the concept of practical significance and are based on professional judgment.

Summary statistics are calculated according to the *Environmental Monitoring Plan* (Woods 2002). The usual summary statistics are the median, which is a measure of central tendency, and interquartile range (IQR), which is a measure of dispersion (variability). However, some tables may present other measures, at the discretion of the responsible analyst.

The median indicates the middle of the data set. That is, half of the measured results are above the median, and half are below. The IQR is the range that encompasses the middle 50% of the data set. The IQR is calculated by subtracting the 25th percentile of the data set from the 75th percentile of the data set. When necessary, the percentiles are interpolated from the data. Different software vendors may use slightly different formulas for calculating percentiles. Radiological data sets that include values less than zero may have an IQR greater than the median. To calculate the median, we require at least four values; to calculate the IQR we require at least six values.

Summary statistics are calculated from values that, if necessary, have already been rounded (such as when units have been converted from pCi to Bq) and are then rounded to an appropriate number of significant digits. The calculation of summary statistics is also affected by the presence of nondetections. A nondetection indicates that no specific measured value is available; instead, the best information available is that the actual value is less than the reporting limit. Adjustments to the calculation of the median and IQR for data sets that include nondetections are described below.

For data sets with all measurements above the reporting limit and radiological data sets that include reported values below the reporting limit, all reported values, including any below the reporting limit, are included in the calculation of summary statistics.

For data sets that include one or more values reported as "less than the reporting limit," the reporting limit is used as an upper bound value in the calculation of summary statistics.

If the number of values is odd, the middle value (when sorted from smallest to largest) is the median. If the middle value and all larger values are detections then the middle value is reported as the median. Otherwise, the median is assigned a less-than (<) sign.

If the number of values is even, the median is halfway between the middle two values (i.e., the middle two when the values are sorted from smallest to largest). If both of the middle two values and all larger values are detections, then the median is reported. Otherwise, the median is assigned a less-than sign.

If any of the values used to calculate the 25th percentile is a nondetection, or any values larger than the 25th percentile are nondetections, then the IQR cannot be calculated and is not reported.

The median and the IQR are not calculated for data sets having no detections.

REPORTING UNCERTAINTY IN DATA TABLES

The measurement uncertainties associated with results from analytical laboratories are represented in two ways. The first of these, significant digits, relates to the resolution of the measuring device. For example, if an ordinary household ruler with a metric scale is used to measure the length of an object in centimeters, and the ruler has tick marks every tenth centimeter, then the length can reliably and consistently be measured to the nearest tenth of a centimeter (i.e., to the nearest tick mark). However, an attempt to be more precise is not likely to yield reliable or reproducible results, because it requires a visual estimate of a distance between tick marks. The appropriate way to report such a measurement would be, for example, "2.1 cm." This would indicate that the "true" length of the object is nearer to 2.1 cm than to 2.0 cm or 2.2 cm (i.e., between 2.05 and 2.15 cm). This result is said to have two significant digits. Although not explicitly stated, the uncertainty is considered to be ± 0.05 cm. A more precise measuring device might

be able to measure an object to the nearest one-hundredth of a centimeter; in that case a value such as "2.12 cm" might be reported. This value would have three significant digits and the implied uncertainty would be ± 0.005 cm. A result reported as "3.0 cm" has two significant digits. That is, the trailing zero is significant, and implies that the true length is between 2.95 and 3.05 cm; closer to 3.0 than to 2.9 or 3.1 cm.

When performing calculations with measured values that have significant digits, all digits are used. The number of significant digits in the calculated result is the same as that of the measured value with the fewest number of significant digits.

Most unit conversion factors do not have significant digits. For example, the conversion from milligrams (mg) to micrograms (μg) requires multiplying by the fixed (constant) value of 1000. The value 1000 is exact; it has no uncertainty and therefore the concept of significant digits does not apply.

The other method of representing uncertainty is based on random variation. For radiological measurements, there is variation due to the random nature of radioactive decay. As a sample is measured, the number of radioactive decay events is counted, and the reported result is calculated from the number of decay events that were observed. If the sample is recounted, the number of decay events will almost always be different—because radioactive decay events occur randomly. Uncertainties of this type are reported in this volume as 2σ uncertainties. A 2σ uncertainty represents the range of results expected to occur approximately 95% of the time, if a sample were to be recounted many times. A radiological result reported as, for example, " 2.6 ± 1.2 Bq/g" would indicate that with approximately 95% confidence, the "true" value is in the range 1.4 to 3.8 Bq/g (i.e., 2.6 - 1.2 = 1.4 and 2.6 + 1.2 = 3.8).

The concept of significant digits applies to both the radiological result and its uncertainty. So, for example, in a result reported as " 2.6 ± 1.2 ", both the measurement and its uncertainty have the same number of significant digits, that is, two. When expanding an interval reported in the " \pm " form, for example " 2.4 ± 0.44 ", to a range of values, the rule described above for calculations involving significant digits must be followed. For example, 2.4 - 0.44 = 1.96. However, the measurements 2.4 and 0.45 each have two significant digits, so 1.96 must be rounded to two significant digits, i.e., to 2.0. Similarly, 2.4 + 0.44 = 2.84, and this must be rounded to 2.8. Therefore, a measurement reported as " 2.4 ± 0.44 Bq/g" would represent an interval of 2.0 to 2.8 Bq/g.

When rounding a value having a final digit of "5", the software that prepared the tables follows IEEE Standard 754-1985, which is "go to the even digit". For example, 2.45 would round down to 2.4, and 2.55 would round up to 2.6.

QUALITY ASSURANCE PROCESS FOR THE ENVIRONMENTAL REPORT

Unlike the preceding sections, which focused on standards of accuracy and precision in data acquisition and reporting, the following discussion deals with procedures used to ensure the content of this report maintained accuracy through the publication process. Because publication of a large, data-rich document like this site annual environmental report involves many operations and many people, the chances of introducing errors are great. At the same time, ensuring quality is more difficult because a publication is less amenable to the statistical processes used in standard quality assurance methods.

The QA procedure used for this report concentrated on the tables and figures and enlisted authors, contributors, and technicians to check the accuracy of sections other than those they had authored or contributed to. In 2003, LLNL staff checked the tables and figures in the report as well as the data tables provided in the report CD.

Checkers were assigned figures and tables and given a copy of each item they were to check along with a quality control form to fill out as they checked the item. Items to be checked included figure captions and table titles for clarity and accuracy, data accuracy and completeness, figure labels and table headings, units, significant digits, and consistency with text.

When checking numerical data, checkers randomly selected 10% of the numbers and compared them to values in the hard copy reports. If all 10% agreed with the hard copy reports, further checking was considered unnecessary. If there was disagreement, the checker compared another 10% of the data with the database values. If more errors were found, the entire table or illustration had to be checked against the data in the database. A coordinator guided the process to ensure that forms were tracked and the proper approvals were obtained. Completed quality control forms and the corrected figures or tables were returned to the report editors, who were responsible for ensuring that changes, with the agreement of the original contributor, were made.